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Upper Jurassic evaporites of the southwestern slope of East European Platform

ELENA V. KHMELEVSKA

Institute of Geology and Geochemistry of Combustible Minerals, National Academy of Sciences of Ukraine, Naukova 3a, 290053 Lviv, Ukraine

Abstract. Upper Jurassic evaporite sequences along the southwestern slopes of East European Platform consist of interbedded dolomites, dolomitic limestones, anhydrite and siliciclastic rocks, and in Predobrogea also of gypsum and rock salt. The rock salt contains chevron and recrystallized halite with specific fluid inclusions in each type. The inclusions have a chloride chemical composition, with the ratios of sodium, potassium and magnesium chlorides similar to those in the modern seawater saturated to the corresponding stage, and differed only by $CaCl_2$ content. Maximum potassium content in brine inclusions in halite is 15.5 g/l and indicates that the concentration of brine in the basin did not reach the stage of potash sedimentation.

Key words: Jurassic, evaporites, rock salt, brine, inclusion, East European Platform.

Introduction

Upper Jurassic evaporite deposits are widespread along the southwestern slope of the East European Platform in Poland, Ukraine, Moldova and Romania (Fig. 1). They consist of interbedded dolomites, dolomitic limestones, anhydrite and siliciclastic rocks, and in Predobrogea also of gypsum and rock salt. In south-eastern Poland these deposits belong to the Ruda Lubycka series of Kimmeridgian age and are subdivided into two parts. The lower one is 140 m thick and the upper one is 100 m thick (Niemczycka, 1976). In the Fore-Carpathian region of Ukraine sulfate-carbonate deposits are distinguished in the Rava Russka series that is 20 to 250 m thick. The thickness of dolomite layers ranges from 1 to 40 m and of anhydrites from several cm to 7 m (Dulub *et al.*, 1986). In Predobrogea region (in Ukraine and Moldova) Kimmeridgian evaporites in the Kongazsky series have a total thickness of 15-445 m (Garetski, 1985). The series contains terrigenous rocks, limestones, dolomites, anhydrite, gypsum and rock salt.

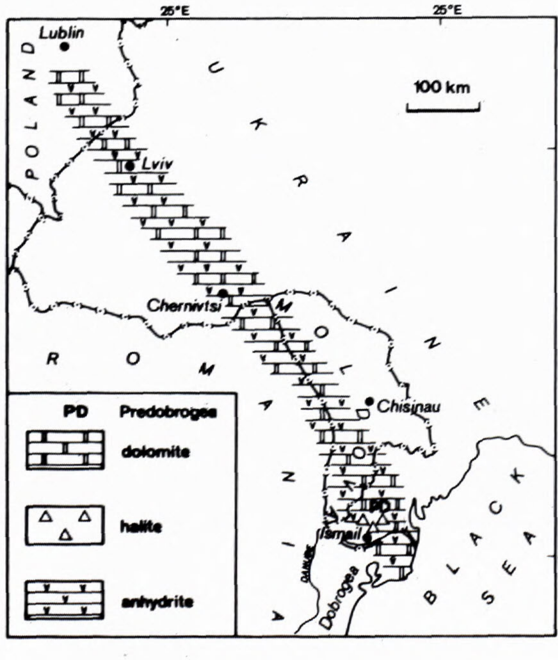

Fig. 1 Schematic map of distribution of Upper Jurassic evaporites, south-western slope of East European Platform.

Dolomites and sulfates

Sulfate and carbonate rocks all over the region are characterized by similar features. Dolomites are grey, light-grey, or brown fine-grained massive rocks. They are composed of dolomite crystals with average sizes of 0.01-0.02 mm, and many dolomites contain silt-sized quartz, plagioclase and muscovite and clay-sized mica and chlorite. The authigenic minerals in dolomites are pyrite, anhydrite and celestite. The latter often forms thin layers in dolomites, where the content of Sr reaches 3% (Khmelevska, 1988). Anhydrites are white, light- and dark-grey, brown and commonly multicoloured, fine-grained, massive rocks. They contain 97-99% of calcium sulfate. Among the admixtures are terrigenous and authigenic quartz, authigenic pyrite, dolomite, calcite, magnesite, and hematite. In the upper part of the Ruda Lubycka series crystals of fluorite were found (Radlicz, 1975). Many anhydrites in Predobrogea contain large inclusions (up to 3-4 cm) of carbonized detrital organic matter. In addition to anhydrite, anhydrite breccia and mixed dolomite-anhydrite and gypsum-anhydrite rocks are also present in the section. Gypsum in the Fore-Carpathian region has been described by Anastasieva (1958) in the Rawa Russka series, developed on Volyn' and Podolia at the depth of 600-1000 m. They have a restricted distribution in carbonate deposits and form the layers up to 1 m thick. In the rest of West Ukraine and in Poland gypsum rocks have not been found. In Predobrogea, gypsum is widespread in the Kongazsky series. It is fine-grained and coarsely-crystalline, blue, grey, brown and yellow in colours and forms of pods, veins and layers in anhydrites (Khmelevska, 1990).

Rock salt

Rock salt occurs only in Predobrogea near Izmail and is represented by white, grey, or pink medium- and coarse-grained halite. Its thickness is about 78 m (Tiuremina & Khmelevska,1990). The NaCl content in rock salt ranges from 93 to 98% and contains authigenic anhydrite, calcite, dolomite, quartz, celestite, fluorite, and pyrite. Bromine content in the rock salt ranges from 0.0027% to 0.0063% and averages 0.0035%. In comparison to experimentally established content of this element (0.0068%) during the initial stage of halite precipitation (Valiashko, 1962), it is depleted. The value of Br·1000/Cl coefficient ranges from 0.038 to 0.10 and in average is 0.058. The decreased content of bromine and a low value of Br·1000/Cl coefficient may be caused by a specific chemical composition of the salt-forming solutions. Valiashko *et al.* (1976) showed that the presence of $CaCl_2$ and $MgCl_2$ in brine could significantly decrease the ability of bromine to enter into the crystalline lattice of halite.

Fluid inclusions

Thermobarogeochemical investigation showed that the rock salt is composed of sedimentary and recrystallized halite. The first contains chevron and hopper crystals with primary fluid inclusions 5-10 to 100-120 μm across. Inclusions have a cubic shape; locally they contain a solid phase represented by anhydrite or pyrite. Ultramicrochemical analysis of fluid inclusions revealed that they have a Na^+-K^+-Ca^{2+}-Mg^{2+}-Cl^--composition (Fig. 2). The potassium content ranges from 5.8 to 15.5 g/l (average is 7.9 g/l). Seawater was the main source of this element in the evaporite-forming process. At the initial stage of halite crystallization the concentration of potassium in the salt-forming basin of Predobrogea was 5-6 g/l. These values correspond to those experimentally established in seawater saturated to the stage of halite precipitation (Valiashko, 1962). During salt crystallization in the basin the concentration of potassium increased to 15 g/l, but such an increase was not gradual. Probably, periodic dilution of the brine led to decrease of potassium content and prevented it from reaching high levels. The concentration of calcium in the brine ranged from 8.5 to 11.8 g/l (average was 10.5 g/l); and of magnesium from 7.9 to 30.5 g/l (average was 13.0 g/l). The total dissolved solid content of the brine was 320-350 g/l.

I have determined the composition of brine inclusions in halite from the lowest part of the salt deposit in Predobrogea. This composition was, on whole, very close to that of modern seawater saturated to the stage of halite precipitation (Table 1). The main difference was in the presence of $CaCl_2$ and in the absence of $MgSO_4$ in salt-forming brine of Predobrogea, that, possibly, was caused by the evolution of the chemical composition of seawater during the Phanerozoic (Kovalevich, 1990). Recrystallized halite is widespread in the salt deposit. It fills the space between relics of zoned grains of sedimentary halite and occurs as separate grains or thin layers. It contains fluid and solid inclusions, rarely two-phase ones (with solid+fluid; fluid+solid phase). Inclusions have different shapes, their sizes range from 20 to 1300 μm. The solid phase in two-phase inclusions consists mainly of xenogenic anhydrite. Solid inclusions are anhydrite, carbonates, quartz and pyrite. Ultramicrochemical analysis of brine inclusions in recrystallized halite shows that they also have a Na^+-K^+-Mg^{2+}-Ca^{2+}-Cl^--composition (Fig. 2). The content of major elements differs from those in sedimentary halite. The concentration of potassium ranges from 1.0 to 12.5 g/l (average 4.6 g/l); of calcium from 8.3-36.0 (average 20.6g/l); and of magnesium from 13.0-39.5 g/l (average 26.9 g/l) (Khmelevska, 1993). Thus, the recrystallization of salt took place under the influence of residual chloride solutions that were buried in soft sediment. The subordinate role of recrystallized halite in salt deposit and the insignificant difference in chemical composition of solutions in fluid inclusions from sedimentary and recrystallized halite suggest that fast postsedimentary alteration of salt sediment was terminated during early diagenesis.

The studied halite does not contain gas inclusions; the gases are dissolved in brine inclusions. The total gas saturation of solutions has been determined by method of Petrichenko (1973). Its value ranges from 1.5 to 9.0 ml/l and in the samples from the bottom of the salt layer is 4.0 ml/l. Such a quantity of dissolved gases could be caused

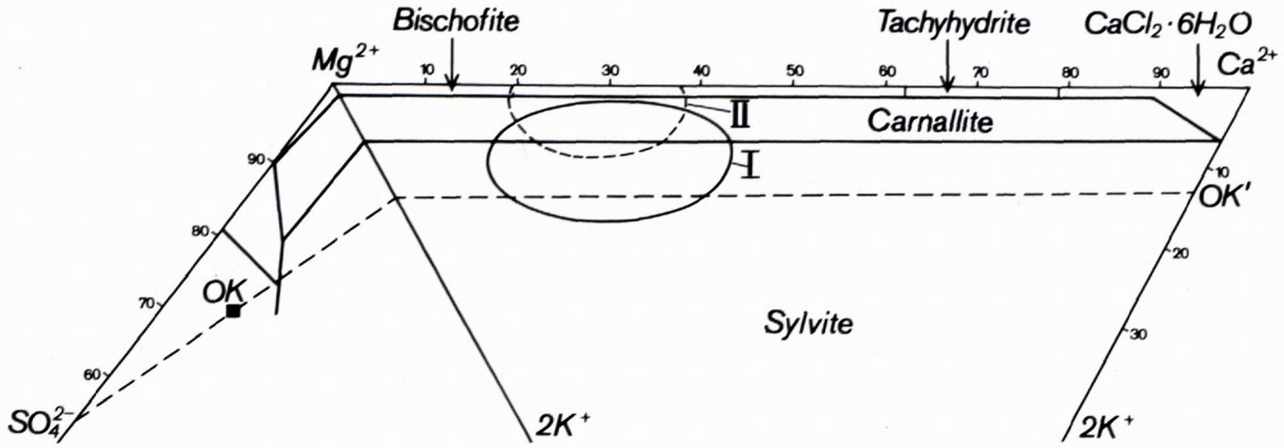

Fig. 2 The brine composition in the Predobrogean evaporite basin on the Valiashko (1962) diagram; I - the field of brine composition during halite sedimentation; II - the field of brine composition during diagenesis. OK - the composition of salt-forming solutions of marine origin; OK-OK' - the line of metamorphism of marine solution.

Table 1. The content of major ions and salts in sea water of different saturations (after Valiashko, 1962) and in brine inclusions of sedimentary halite from the lower part of Predobrogean salt series

Type of seawater	Content of ions and salts, g/l										
	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	$CaCl_2$	$MgCl_2$	NaCl	KCl	$MgSO_4$
Normal seawater	0.43	1.3	11.3	0.4	20.1	2.9	-	3.385	27.6	0.76	2.305
At the beginning of halite precipitation	0.42	15.5	104.3	3.3	191.2	21.0	-	33.4	214.1	5.2	21.0
At the beginning of halite precipitation in the Predobrogean basin	9.7	13.0	90.0	5.2	166.6	0.5	26.8	59.0	214.5	9.3	-

by low pressure, that occurred in the salt-forming basin at the depth of 16-20 m. The presence of only one-phase fluid inclusions (without daughter crystal and gas bubble) suggest that the temperature of brine in the basin did not exceed 40°C.The gas mixture consists of N_2 (72.7 - 83.3 vol%), CO_2 (10.0 - 18.2 vol%), and CH_4 (4.4 - 9.1 vol%). The absence of solid hydrocarbons in the gas mixture shows a low possibility for oil discoveries in underlying deposits.

Conclusions

The analyses of brine inclusions in halite show the marine origin of this rock salt. The chloride composition of solutions and the absence of significant amounts of SO_4 and HCO_3 demonstrate that the salt deposits do not contain sulfate salts and soda. The maximum content of potassium in brine inclusions in sedimentary halite is 15.5 g/l and according to Petrichenko *et al.* (1976) is typical for deposits that do not contain potash salts. The maximum concentration of KCl in solutions (29.6 g/l) is only 30% of what is necessary for precipitation of KCl as a solid phase. The calculations show that the Predobrogea rock salt has no potash-bearing indications. This is also confirmed by mineralogical and geochemical data which show that the rock salt is composed of NaCl (up to 98%) and the amount of KCl is less than 0.6%. Among the authigenic minerals in the water-insoluble part of rock salt anhydrite prevails, dolomite is common, but magnesite is completely lacking. As the latter is the indicator of higher stages of evaporation, the brine, obviously, did not reach them during its evolution. Also the bromine content in the rock salt corresponds to the initial stage of halite precipitation. Thus the economic interest in these deposits may be related only to the rock salt itself.

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